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ELECTRICAL CONDUCTIVITY OF SALT MELTS IN
A LiCl-BaCl₂ SYSTEM

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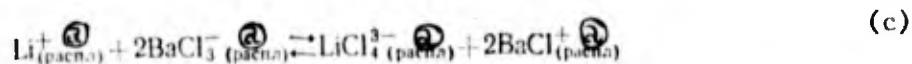
The LiCl-BaCl₂ system is interesting in that the lithium and barium cations are very close in their ionic moments

$$\left(\frac{e_{\text{Li}^+}}{r_{\text{Li}^+}} = 1.47; \frac{e_{\text{Ba}^{++}}}{r_{\text{Ba}^{++}}} = 1.40 \right), \quad (\text{a})$$

but differ significantly in their radii

$$(r_{\text{Li}^+} = 0.68 \text{ \AA}; r_{\text{Ba}^{++}} = 1.43 \text{ \AA}) \quad (\text{b})$$

and charges. It has been shown in a work studying CsCl-BaCl₂ melts [1] how substitution by low-movement complex BaCl⁺ cations in the second coordination sphere of the elementary Cs⁺ cation, which participates in transmission of electricity due to Stokes shift, influences electrical conductivity. In LiCl-BaCl₂ melts, one may expect replacement of elementary lithium cations by complex BaCl⁺ ions as the concentration of barium chloride increases. On the strength of the proximity of the polarizing effects of Li⁺ and Ba²⁺, it may be expected that the equilibrium of the



Key: a. fused.

reaction will shift noticeably with change in temperature. Inasmuch as elementary and complex ions participate in various ways in transmission of electricity, temperature changes must exert a system-specific influence on a system's electrical conductivity.

In order to measure electrical conductivity we used methods described earlier [1, 2]. We conducted experiments in hermetic cells whose gaseous

space above the melts was filled with pure argon. The cell's constant, determined according to pure fused potassium chloride, was equal to 27.278 cm^{-1} .

The electrical conductivity of fused LiCl-BaCl_2 mixtures containing 22.4; 35.6; 47.6; 65.0; 78.4 and 89.5 mol. % BaCl_2 was measured. Twelve-15 experimental points were obtained for each melt within a $800-1000^\circ\text{C}$ temperature interval. Expressions for the temperature dependence of specific electrical conductivity ($\Omega^{-1}\cdot\text{cm}^{-1}$) was calculated by the method of least squares for melts of the specified compositions:

BaCl_2 , mol. %		
0	$\kappa = +0.528 + 11.25 \cdot 10^{-3}t - 4.554 \cdot 10^{-6}t^2 \pm 0.008$	
22.4	$\kappa = -0.790 + 6.416 \cdot 10^{-3}t + 0.02$	
35.6	$\kappa = -1.541 - 0.786 \cdot 10^{-3}t + 4.127 \cdot 10^{-6}t^2 \pm 0.006$	
47.6	$\kappa = -1.207 - 3.974 \cdot 10^{-3}t + 6.070 \cdot 10^{-6}t^2 \pm 0.007$	(d)
65.0	$\kappa = -1.325 + 5.763 \cdot 10^{-3}t \pm 0.008$	
78.4	$\kappa = -2.306 + 5.187 \cdot 10^{-3}t \pm 0.007$	
89.5	$\kappa = -1.477 + 3.911 \cdot 10^{-3}t \pm 0.007$	
100.0	$\kappa = +0.636 + 1.533 \cdot 10^{-6}t^2 \pm 0.008$	

The specific electrical conductivity of melts decreases monotonously as BaCl_2 concentration increases and reaches a minimum of value with pure barium chloride (Fig. 1).

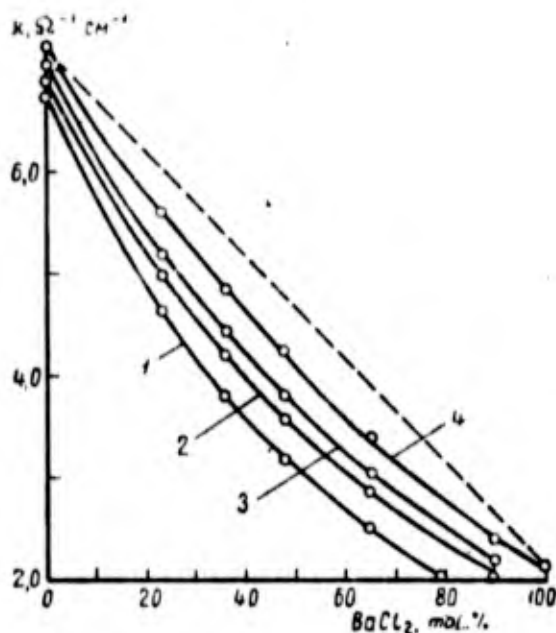


Fig. 1. Isotherms of specific electrical conductivity in LiCl-BaCl_2 melts.

Key: 1. 1120; 2. 1180; 3. 1210; 4. 1270°K.

Molar electrical conductivity may be calculated using data from a work [3] on the density of $\text{LiCl}-\text{BaCl}_2$ fused-salt mixtures. For all of the melts studied, conductivity varied with temperature according to the equation

$$\lg \Lambda = A - \frac{B}{T} \quad (e)$$

The table presents values of constants A and B and energy of activation of molar electrical conductivity, E_A .

Table. Values of A and B in equations of the temperature dependence of molar electrical conductivity and energy of activation.

$\text{BaCl}_2, \text{ mol.}\%$	A	B	$E_A, \text{ cal/mole}$
0	2,7158	450,9	2080
22,4	3,1151	973,6	4180
35,6	3,2557	1170,6	5390
47,6	3,4131	1391,3	6400
65,0	3,3724	1393,5	6420
78,4	3,4129	1495,3	6880
89,4	3,2386	1333,2	6130
100	3,0876	1172,8	5400

In all of the composition interval the molar electrical conductivity of $\text{LiCl}-\text{BaCl}_2$ fused salts is higher in pure fused barium chloride. This indicates that it is determined mainly by Stokes shift of very mobile elementary Li^+ cations in the second coordination spheres. Isotherms of molar electrical conductivity are shown in Fig. 2. At 1180°K the isotherm is very close to the additive (dotted line). At higher temperatures the isotherms begin to deviate from additivity toward greater values of molecular electrical conductivity, while at lower temperatures they begin to deviate toward lesser values.

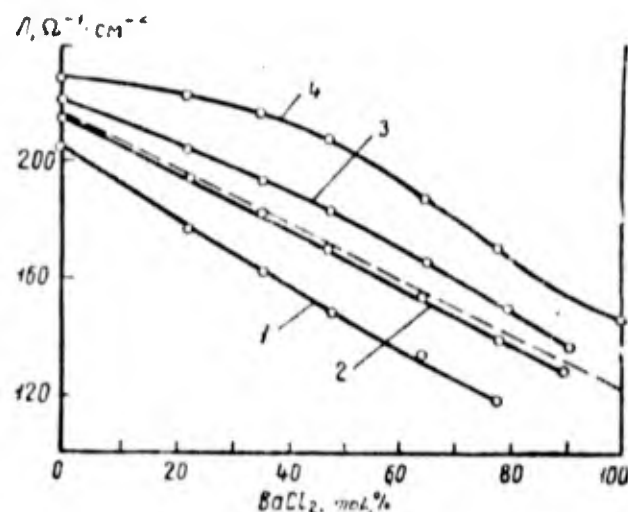


Fig. 2. Isotherms of molar electrical conductivity in LiCl-BaCl₂ melts.

Key: 1. 1120; 2. 1180; 3. 1210; 4. 1270°K.

In CsCl-LiCl [2] and CsCl-BaCl₂ [1] melts, isotherms of molar electrical conductivity had an extreme course with great change in magnitude of electrical conductivity in the first system and with an absolute minimum in the second. In CsCl-LiCl melts containing up to 75 mol. % CsCl, elementary Li cations are replaced by significantly less mobile elementary Cs ions in the second coordination sphere. This is accompanied by a great decrease in electrical conductivity, which continues to depend mainly on Stokes shift of cations. In CsCl-BaCl₂ melts, change in composition is accompanied by substantial redistribution between fractions of electrical conductivity connected with Stokes shift of cations in the second coordination sphere and with transfer of chlorine anions between BaCl⁺ and BaCl₃⁻ complexes. It is highly probable that as complexes of BaCl⁺ and BaCl₃⁻ ions are accumulated in LiCl-BaCl₂ melts containing more than 50 mol. % BaCl₂ transfer of the chlorine ion between complexes begins to play an ever more appreciable role. As a result of this electrical conductivity does not decrease with drop in chloride concentration as rapidly as in a CsCl-LiCl system. It is significant that the activation energy of molar electrical conductivity reaches its maximum of value and remains practically constant in fused LiCl-BaCl₂ mixtures containing more than 50 mol. % of barium chloride (Fig. 3.). A similar picture is observed in a change of activation energy of molecular conductivity with melts in the CsCl-BaCl₂ system.

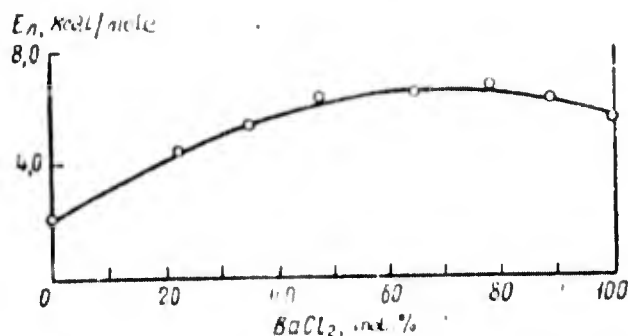
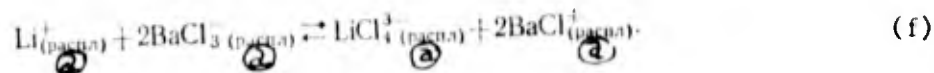


Fig. 3. Change in molecular electrical conductivity activation energy in a LiCl-BaCl₂ fused-salt system.

Deflections of isotherms, tending with increase in temperature toward greater values of molecular electrical conductivity of LiCl-BaCl₂ melts, testify to an increase in its component linked with Stokes shift of elementary cations in the second coordination sphere. The quantity of these cations grows due to leftwards displacement of the equilibrium of the reaction



Key: a. fused.

Conclusions

1. The specific electrical conductivity of LiCl-BaCl₂ melts containing 22.4; 35.6; 47.6; 65.0; 78.4 and 89.5 mol. % BaCl₂ was measured.
2. Expressions were found for temperature dependence of specific and molar electrical conductivity of fused mixtures of lithium and barium chlorides.
3. Deflections of molar electrical conductivity isotherms from additivity go gradually from negative to positive with increase in temperature.

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